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Improved Hydrogen-Sensitive Properties of MISiC Schottky Sensor with Thin NO-Grown Oxynitride as Gate Insulator

J. P. Xu, P. T. Lai, *Member, IEEE*, D. G. Zhong, and C. L. Chan, *Member, IEEE*

Abstract—Thin oxynitride grown in NO at low temperature was successfully used as gate insulator for fabricating MISiC Schottky hydrogen sensors. Response properties of the sensors were compared with other MISiC Schottky sensors with thicker or no oxynitride. It was found that the thin oxynitride played an important role in increasing device sensitivity and stability. Even at a low H_2 concentration, e.g., 100-ppm H_2 in N_2 , a significant response was observed, indicating a promising application for detecting hydrogen leakage. Moreover, a rapid and stable dynamic response on the introduction and removal of H_2/N_2 mixed gas was realized for the sensor. Improved interface properties and larger barrier height associated with the thin oxynitride are responsible for the excellent response characteristics. As a result, NO oxidation could be a superior process for preparing highly sensitive and highly reliable MISiC Schottky hydrogen sensors.

Index Terms—Hydrogen sensors, NO, oxynitride, silicon carbide.

I. INTRODUCTION

OVER THE past few years, there has been an increasing interest in the field of gas sensors that can operate in harsh environments such as hot-engine control for aerospace and automobile applications, process-gas monitoring, and leak detection. The requirement of operating in high-temperature environments brought SiC into attention due to its remarkable properties, e.g., outstanding thermal stability enabling operation up to 1000 °C. So far, a large amount of research work on catalytic metal (e.g., Pt, Pd)-insulator (SiO_2)-silicon carbide (MISiC) gas sensors, including MISiC Schottky diodes and MISiC capacitors, has been conducted [1]–[4]. It has been shown that MISiC Schottky diodes are preferably selected as gas sensors due to their much simpler electronic circuitry required for operation [3] and a direct or indirect sensitivity to gases like H_2 , hydrocarbons, CO, NO, and O_2 . Unfortunately, a main failure mechanism of the sensors at high temperatures is failure of the gate insulator due to the mixing of layers and oxide consumption [5], [6], which lead to long-term high-temperature

stability problem of the gas response. Presently, the insulator used in MISiC Schottky hydrogen sensor is a very thin (~ 1 nm) native oxide, or SiO_2 created by various processes such as ozone exposure [7]–[9]. Therefore, it is easy to consume the insulator when intermixing of materials at the metal-oxide and oxide-SiC interfaces occurs due to poor interfacial diffusion barrier (weak Si-Si and Si-O bonds of the oxides). In addition, high interface-state and fixed-charge densities of the oxide greatly degrade the device characteristics, e.g., sensitivity and stability. Therefore, development of a high-quality thin insulator for MISiC Schottky hydrogen sensors becomes a key issue. In this work, a technique of growing thin oxynitride in NO as the thin insulator of MISiC Schottky sensors was developed for the first time, and greatly improved hydrogen response and stability were obtained as compared with MISiC Schottky sensors with thicker or no oxynitride. Relevant results are reported, and physical mechanisms involved are analyzed.

II. EXPERIMENTS

N-type (0001) Si-face 6H-SiC wafers, manufactured by Cree Research, were used in this study. The SiC wafers had a 5- μm epitaxial layer grown on heavily doped substrate. The doping level of the epitaxial layer was $4 \times 10^{15} \text{ cm}^{-3}$. The wafers were cleaned using the conventional RCA method followed by a 1-min dip in 5% HF to remove the native oxide. The wafers were then loaded into a quartz furnace at required oxidation temperature in N_2 to have good control on the final thickness of thin oxynitrides. Oxidation conditions of MISiC Schottky sensors were 800 °C/7 min and 900 °C/5 min, respectively, both in pure NO ambient (0.5 l/min) to produce thin oxynitrides with about the same thickness (denoted as NOG10 and NOG15, respectively, with the number indicating the thickness t_{ox} of the resulting oxynitride in angstroms measured by ellipsometry). Post-oxidation annealing was done *in-situ* at the oxidation temperature in N_2 (1 l/min) for 5 min. For the purpose of comparison, two other samples were prepared: 1) The wafer was loaded into quartz furnace at 900 °C in N_2 and oxidized at 1100 °C for 4 h in pure NO ambient (0.5 l/min) to form a much thicker oxynitride. Because of the higher oxidation temperature and longer oxidation time, a longer annealing was carried out in N_2 (1 l/min) for 30 min after cooling down in N_2 with a ramping rate of -1 °C/min to 950 °C (denoted as NOG120, i.e., $t_{ox} = 12 \text{ nm}$); 2) no oxynitride was grown on the surface of wafer (denoted as NOG0, i.e., MISiC Schottky sensor). Electrodes of all samples were formed by dc-magnetron sputtering at a substrate temperature of 350 °C, and 200-nm TaSi_x

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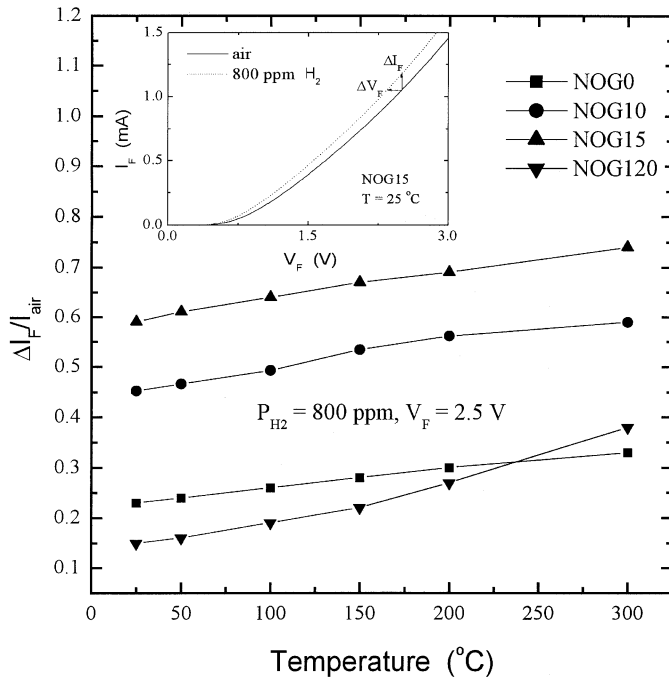


Fig. 1. Temperature dependence of forward-current change ($\Delta I_F / I_{\text{air}}$) of all samples when changing environment from air to 800-ppm H_2 in N_2 under $V_F = 2.5$ V. The inset are the I - V curves of the NOG15 sample in air and 800 ppm H_2 in N_2 at room temperature.

and 400-nm Pt formed an ohmic back contact after etching off the oxide, while 10-nm TaSi_x and 100-nm Pt were deposited through a stainless steel mask, producing a gate electrode with a diameter of 0.5 mm. The samples did not go through any activation procedure for increasing sensitivity [1].

III. RESULTS AND DISCUSSION

Steady-state and transient response measurements were performed in a copper reaction chamber located inside a high-temperature thermostat and connected to a gas flow tube with a regulating valve. The forward current-voltage (I_F - V_F) characteristics of the MISiC Schottky diodes were measured at different temperatures and hydrogen concentrations by HP4145B semiconductor parameter analyzer to examine the hydrogen-sensitive properties of the devices.

Fig. 1 shows the temperature dependency of response signal (current change ΔI_F normalized by corresponding current in air I_{air}) of all samples at V_F of 2.5 V when the chamber environment is changed from air (the reference) to 800-ppm H_2 in N_2 . In fact, ΔI_F is caused by a voltage shift ΔV_F in the H_2 -containing environment, as shown by the I - V curve shift in the inset of Fig. 1. Three points can be summarized from Fig. 1 as follows: 1) Sensitivities of all samples increase as temperature rises, where sensitivities of NOG10 and NOG15 samples with thin oxynitride are obviously higher than those of the NOG0 and NOG120 devices for the whole measured temperature range; 2) the two sensors with thin oxynitride have good response to hydrogen even at room temperature, and it can be found that the sensitivity increases with thickness for thin oxynitrides and has a maximum value for an optimal thickness; 3) for the NOG120 sample, its sensitivity is lower than that of the NOG0 sample at temperatures below 220°C but then exceeds it

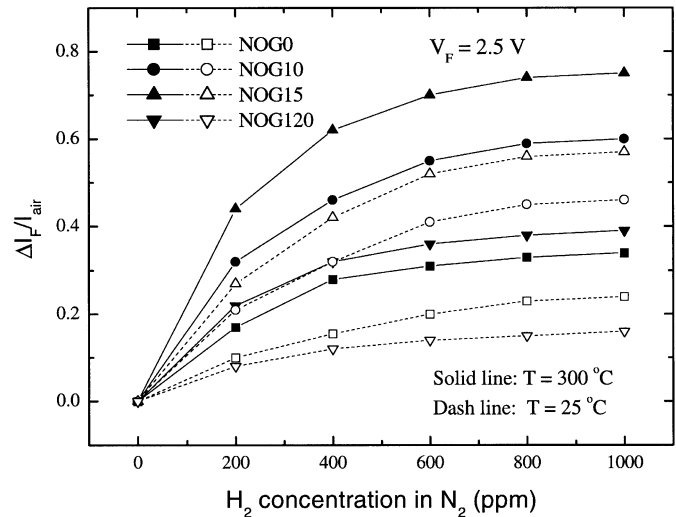


Fig. 2. Forward-current change ($\Delta I_F / I_{\text{air}}$) as a function of hydrogen concentration in N_2 at $T = 25$ and 300°C under $V_F = 2.5$ V.

at higher temperatures. As compared with MSiC Schottky sensors, the higher sensitivity of MISiC Schottky sensors with thin oxynitride can be ascribed to two factors: 1) a remarkable reduction of leakage current in air [10] resulting from improved interface properties for NO-grown oxynitride [11] and 2) the oxynitride-induced larger barrier height associated with thermionic emission providing a wider regime of barrier-height modulation when adsorbed hydrogen atoms diffuse to Pt-oxynitride interface and form a dipole layer [10]. However, when the oxynitride is too thick (NOG120), thermionic emission current through the MISiC Schottky diode is very small, especially at low temperatures, and thus, the current shift under the H_2 -containing environment is small, despite the modulation effect of the barrier height. As temperature increases, thermionic emission current becomes large, and hence, the current shift under the H_2 environment is significant (e.g., $\Delta I_F / I_{\text{air}}$ at 300°C is 2.5 times that at room temperature). This implies that MISiC Schottky sensors with thicker oxynitride probably have good hydrogen response and good stability at higher temperatures. From the above discussion, it can be suggested that the oxynitride thickness is a key factor affecting the sensitivity and stability of MISiC Schottky sensors and has different optimal values for different temperature ranges. It should be noted that higher oxidation temperature can also improve the oxynitride quality and, hence, device sensitivity, although the NOG120 sample with the highest oxidation temperature shows the lowest sensitivity due to the dominant role of its thick oxynitride.

Fig. 2 is the sensor response ($\Delta I_F / I_{\text{air}}$) on exposure to different H_2 concentrations in N_2 at room temperature (25°C) and 300°C under $V_F = 2.5$ V for all the samples. As can be seen, response signals of the sensors increase rapidly at low H_2 concentrations first and then gradually reach saturation at high H_2 concentrations ($> \sim 600$ ppm). Again, the sensors with thin oxynitride (NOG10 and NOG15) exhibit high sensitivity to H_2 in the whole measured range of H_2 concentration with the highest for the NOG15 sample ($t_{\text{ox}} = 1.5$ nm). Even at the lowest measured H_2 concentration of 200-ppm H_2 in N_2 , a substantial response is obviously observed for the NOG15 sample at room temperature.

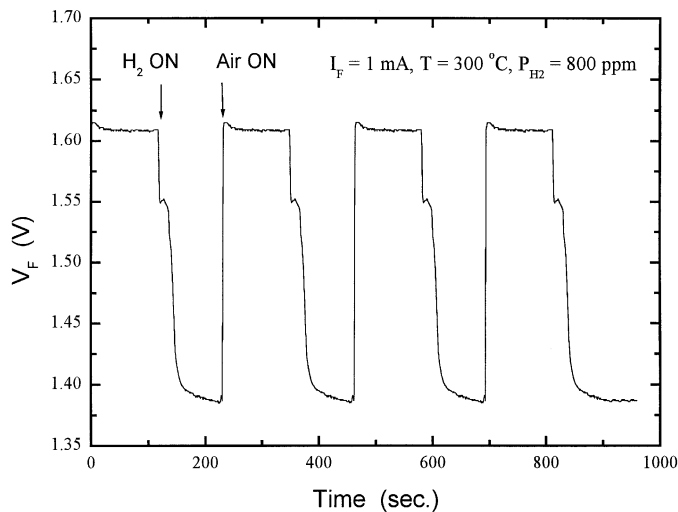


Fig. 3. Forward-voltage (V_F) change of the NOG15 sample at 300 °C on alternate exposure to air and H_2/N_2 mixed gas (800 ppm of H_2) under $I_F = 1$ mA.

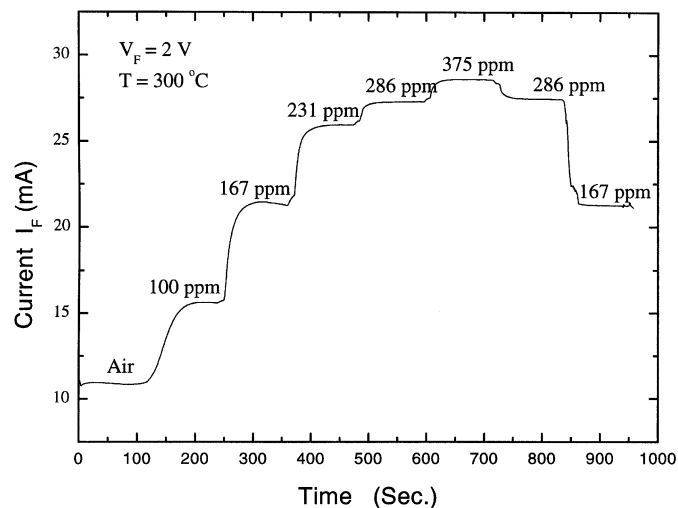


Fig. 4. Response characteristics of the NOG15 sample when continually changing H_2 concentrations in N_2 at 300 °C under $V_F = 2$ V.

The forward-voltage response of the NOG15 sample for a fixed forward current of 1 mA at 300 °C on alternate exposure to air and H_2/N_2 gas with 800 ppm of H_2 is presented in Fig. 3. It can be observed that a rapid and stable response can be obtained for the MISiC Schottky sensor with a thin oxynitride (a larger response is expected if the sample is fully activated [1]). Excellent response to H_2 is further confirmed through continually changing hydrogen concentration, which gives rise to the rapid "ladder" response shown in Fig. 4, even for 100-ppm H_2 concentration in N_2 .

Preliminary testing on the long-term stability of the NOG15 sample was performed for 4 days in H_2/N_2 gas with 800 ppm

of H_2 at 300 °C under $V_F = 2$ V. No obvious response degradation was observed. In fact, the device sensitivity was increased by 0.2%, probably due to a slight activation under the test conditions.

IV. SUMMARY

MISiC Schottky hydrogen sensors with thin NO-grown oxynitride as gate insulator were successfully prepared, and excellent H_2 -sensitive properties were obtained at not only high temperatures but also at room temperature. Experimental results showed that the thin oxynitride was the key factor in affecting sensitivity and stability. Rapid, strong, and stable response on a changing environment was realized for the hydrogen sensor with thin oxynitride as gate insulator. A substantial response to H_2 even at room temperature and low H_2 concentrations provides a potential application for detecting hydrogen leakage. Therefore, it can be suggested that low-temperature NO oxidation is a promising processing step for preparing a high-sensitivity and high-reliability MISiC Schottky hydrogen sensor.

REFERENCES

- [1] A. L. Spetz, P. Tobias, A. Baranzahi, P. Mårtensson, and I. Lundström, "Current status of silicon carbide based high-temperature gas sensors," *IEEE Trans. Electron Devices*, vol. 46, pp. 561–566, Mar. 1999.
- [2] C. K. Kim, J. H. Lee, Y. H. Lee, N. I. Cho, and D. J. Kim, "A study on a platinum-silicon carbide Schottky diodes as a hydrogen gas sensor," *Sensors Actuators B*, vol. 66, pp. 116–118, 2000.
- [3] A. L. Spetz, P. Tobias, L. Unéus, H. Svenningstorp, and L.-G. Ekedahl, "High temperature catalytic metal field effect transistors for industrial application," *Sens. Actuators B*, vol. 70, pp. 67–76, 2000.
- [4] H. Svenningstorp, B. Widén, P. Salomonsson, L.-G. Ekedahl, I. Lundström, P. Tobias, and A. L. Spetz, "Detection of HC in exhaust gases by an array of MISiC sensors," *Sens. Actuators B*, vol. 77, pp. 177–185, 2001.
- [5] A. L. Spetz, D. Schmeisser, A. Baranzahi, B. Walivaara, W. Gopel, and I. Lundström, "X-ray photoemission and auger electron spectroscopy analysis of fast responding activated metal oxide silicon carbide gas sensors," *Thin Solid Films*, vol. 299, pp. 183–189, 1997.
- [6] E. Danielsson, C. I. Harris, C.-M. Zetterling, and M. Ostling, "Thermal stability of sputtered TiN as metal gate on 4H-SiC," in *Proc. 7th Int. Conf. Silicon Carbide, III-Nitrides Related Materials*. Stockholm, Sweden: Trans Tech, 1997, vol. 2, pp. 805–808.
- [7] L.-Y. Chen, G. W. Hunter, P. G. Neudeck, G. Bansal, J. B. Petit, and D. Knight, "Comparison of interfacial and electronic properties of annealed Pd/SiC and Pd/SiO₂/SiC Schottky diodes," *J. Vac. Sci. Technol. A*, vol. 15, pp. 1228–1234, 1997.
- [8] S. Zangoie, H. Arwin, I. Lundstrom, and A. L. Spetz, "Ozone treatment of SiC for improved performance of gas sensitive Schottky diodes," in *Mat. Sci. Forum*, vol. 338–342, 2000, pp. 1085–1088.
- [9] P. Tobias, A. Baranzahi, A. L. Spetz, O. Kordina, E. Janzén, and I. Lundström, "Fast chemical sensing with metal-insulator silicon carbide structures," *IEEE Electron Device Lett.*, vol. 18, pp. 287–289, June 1997.
- [10] W. C. Liu, H. J. Pan, H. I. Chen, K. W. Lin, and S. Y. Cheng, "Hydrogen-sensitive characteristics of a novel Pd/InP MOS Schottky diode hydrogen sensor," *IEEE Trans. Electron Devices*, vol. 48, pp. 1938–1944, Sept. 2001.
- [11] S. Chakraborty and P. T. Lai, "MOS characteristics of NO-grown oxynitrides on n-type 6H-SiC," *Microelectron. Reliab.*, to be published.